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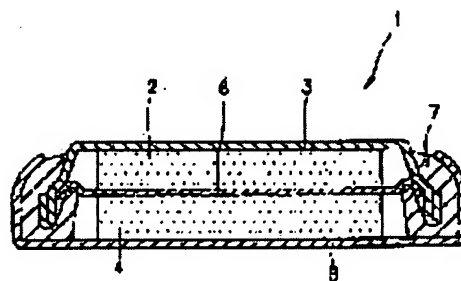
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(54) POSITIVE ELECTRODE ACTIVE MATERIAL, NONAQUEOUS ELECTROLYTE BATTERY, AND THEIR MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material having characteristics of both the Ni composite oxide particles with a large energy density and LiFePO<sub>4</sub> particles with the capacity deterioration remaining lesser at the time of charging.

SOLUTION: The surfaces of particles expressed by the general formula LiNi<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub>, (where M is element(s) containing at least one of Al, B, Co) are covered with particulates expressed by the general formula LiFePO<sub>4</sub>.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to those manufacture approaches at the positive active material which used lithium nickel complex oxide and a nonaqueous electrolyte cell, and a list.

[0002]

[Description of the Prior Art] Research of the rechargeable battery in which a recharge is possible in recent years as a power source which can be used conveniently [ for a long time ] and economically with the rapid progress of various electronic equipment is advanced. As a typical rechargeable battery, the lead accumulator, the alkaline battery, the lithium secondary battery, etc. are known. Especially the lithium secondary battery has advantages, such as high power and a high energy consistency. The above-mentioned lithium secondary battery consists of the positive electrode and negative electrode in which ejection and insertion are possible, and nonaqueous electrolyte reversibly in a lithium ion.

[0003] the conductive polymer and stratified compounds (carbon material metallurgy group oxide etc.) with which a metal lithium, a lithium alloy, and \*\* CHIUMU were generally doped as a negative-electrode active material -- the conductive polymer and stratified compounds (carbon material metallurgy group oxide etc.) which were made to coexist with the compound which contains beam CHIUMU again are used.

[0004] On the other hand, a metallic oxide, metallic sulfide, or a polymer is used for positive active material, for example, non-\*\* lithium compounds, such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{NbSe}_2$ , and  $\text{V}_2\text{O}_5$ , and a multiple oxide like  $\text{LiMO}_2$  ( $\text{M}=\text{Co}$ , nickel, Mn, Fe, etc.) which has already contained the lithium are proposed.

[0005] The solution made to dissolve a \*\* CHIUMU salt in an aprotic organic solvent like propylene carbonate as the electrolytic solution is used.

[0006] Furthermore, although high polymer films, such as polypropylene, are used as a separator, it must be made as thin as possible from the point of lithium ion conductivity and an energy density in this case. Usually, a separator 50 micrometers or less is considered to be practical use. The above positive electrodes, a negative electrode, and the separator which intervened among both and the cell which consisted of the electrolytic solutions can be used as a rechargeable battery in which charge and discharge are possible.

[0007]

[Problem(s) to be Solved by the Invention] nickel system positive active material which high-capacity-izes a lithium secondary battery has more amounts of lithiums from which it escapes at the time of charge than the conventional Co system positive active material. Therefore, in nickel system positive active material, the stability of structure will be lost and capacity degradation at the time of charge is observed. On the other hand,  $\text{LiFePO}_4$  was excellent in the structural stability at the time of charge, and although there was little capacity degradation, its energy density was small and it had the point that an activity independently was difficult.

[0008] It was searched for the technique of making  $\text{LiFePO}_4$  adhere to the front face of nickel multiple

oxide particle, in order to excel in the stability at the time of the charge which has these both advantage and to obtain the positive active material which is high capacity. However, the effective approach was not yet found out.

[0009] This invention is proposed in view of the conventional actual condition which was mentioned above, and aims at offering the positive active material which has the property of both nickel multiple oxide particle with a large energy density, and  $\text{LiFePO}_4$  particle with small capacity degradation at the time of charge, the nonaqueous electrolyte cells using the positive active material, and those manufacture approaches.

[0010]

[Means for Solving the Problem] Positive active material of this invention is characterized by coming to cover the front face of the particle expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M is an element which contains a kind at least among aluminum, B, and Co among a formula.) with the particle expressed with a general formula  $\text{LiFePO}_4$ .

[0011] In the positive active material of this invention which was mentioned above, since it comes to cover the front face of the particle expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  with the particle expressed with a general formula  $\text{LiFePO}_4$ , it becomes what has the property of both nickel multiple oxide particle with a large energy density, and  $\text{LiFePO}_4$  particle excellent in structural stability.

[0012] Moreover, the nonaqueous electrolyte cell of this invention is equipped with the nonaqueous electrolyte which intervenes between the positive electrode which has positive active material, the negative electrode which has a negative-electrode active material, and the above-mentioned positive electrode and the above-mentioned negative electrode, and the above-mentioned positive active material is characterized by coming to cover the front face of the particle expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M is an element which contains a kind at least among aluminum, B, and Co among a formula.) with the particle expressed with a general formula  $\text{LiFePO}_4$ .

[0013] By the nonaqueous electrolyte cell concerning this invention which was mentioned above, since it comes to cover the front face of a particle where positive active material is expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  with the particle expressed with a general formula  $\text{LiFePO}_4$ , it becomes what has the property of both nickel multiple oxide particle with a large energy density, and  $\text{LiFePO}_4$  particle excellent in structural stability. And the nonaqueous electrolyte cell of this invention using such positive active material becomes what combines high capacity and a high charge-and-discharge cycle property.

[0014] Moreover, the manufacture approach of the positive active material of this invention be stir so that the particle express with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M's be an element which contain a kind at least among aluminum, B, and Co among a formula.), and the particle express with a general formula  $\text{LiFePO}_4$  may be mix and particle temperature's (T's)'s may serve as range which be  $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ , and be characterize by to cover the front face of the above-mentioned particle with the above-mentioned particle.

[0015] By the manufacture approach of positive active material which was mentioned above, the positive active material on which the particle expressed with the front face of the particle expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  by the general formula  $\text{LiFePO}_4$  was made to put by specifying the particle temperature at the time of stirring a mixed particle is obtained.

[0016] Moreover, the manufacture approach of the nonaqueous electrolyte cell of this invention It is the manufacture approach of the nonaqueous electrolyte cell equipped with the nonaqueous electrolyte which intervenes between the positive electrode which has positive active material, the negative electrode which has a negative-electrode active material, and the above-mentioned positive electrode and the above-mentioned negative electrode. In case the above-mentioned positive active material is compounded, it is general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M is an element which contains a kind at least among aluminum, B, and Co among a formula.). The particle expressed and the particle expressed with a general formula  $\text{LiFePO}_4$  are mixed, and it is characterized by covering the front face of the above-mentioned particle with the above-mentioned particle, and using it as positive active material by stirring so that particle temperature (T) may serve as range which is  $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ .

[0017] By the manufacture approach of the nonaqueous electrolyte cell concerning this invention which

was mentioned above, the positive active material on which the particle expressed with the front face of the particle expressed with general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  by the general formula  $\text{LiFePO}_4$  was made to put by specifying the particle temperature at the time of stirring a mixed particle is obtained. And by the manufacture approach of the nonaqueous electrolyte cell of this invention using such positive active material, the nonaqueous electrolyte cell which combines high capacity and a high charge-and-discharge cycle property is obtained.

[0018]

[Embodiment of the Invention] The example of 1 configuration of the nonaqueous electrolyte cell which applied this invention is shown in drawing 1. This nonaqueous electrolyte cell 1 is equipped with the separator 6 allotted between a negative electrode 2, the negative-electrode can 3 which holds a negative electrode 2, the positive electrode 4, the positive-electrode can 5 which holds a positive electrode 4, and a positive electrode 4 and a negative electrode 2, and an insulating gasket 7, and it comes to fill up nonaqueous electrolyte in the negative-electrode can 3 and the positive-electrode can 5.

[0019] A negative electrode 2 consists for example, of a metal lithium foil used as a negative-electrode active material. Moreover, in using the ingredient in which a dope and a dedope of a lithium are possible as a negative-electrode active material, it comes to form the negative-electrode active material layer to which a negative electrode 2 contains the above-mentioned negative-electrode active material on a negative-electrode charge collector. As a negative-electrode charge collector, a nickel foil etc. is used, for example.

[0020] As a negative-electrode active material in which a dope and a dedope of a lithium are possible, the conductive polymer and stratified compounds (carbon material metallurgy group oxide etc.) with which the metal lithium, the lithium alloy, and the lithium were doped are used.

[0021] As a binder contained in a negative-electrode active material layer, the well-known resin ingredient usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used.

[0022] The negative-electrode can 3 holds a negative electrode 2, and serves as an external negative electrode of the nonaqueous electrolyte cell 1.

[0023] It comes to form the positive-active-material layer to which a positive electrode 4 contains positive active material on a positive-electrode charge collector. As a positive-electrode charge collector, aluminium foil etc. is used, for example.

[0024] Here, in this invention, the thing which comes to cover with  $\text{LiFePO}_4$  particle the front face of a particle with which it is expressed general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M is an element which contains a kind at least among aluminum, B, and Co among a formula.) as positive active material is used.

[0025] Although the energy density was large, nickel multiple oxide had many amounts of lithiums from which it escapes at the time of charge, and as mentioned above, in order that structure might destabilize, it had the problem of causing capacity degradation. On the other hand,  $\text{LiFePO}_4$  was excellent in the structural stability at the time of charge, and although there was little capacity degradation, its energy density was small and it had the problem that an activity independently was difficult.

[0026] By lithium desorption at the time of charge, the capacity degradation phenomenon by structure destruction produces nickel multiple oxide which structure destabilized in an interface with the nonaqueous electrolyte inside a cell. Especially, in an elevated temperature (40 degrees C - 60 degrees C), degradation extent is large. If that front face is thermally reformed to stable  $\text{LiFePO}_4$  to this nickel multiple oxide, capacity degradation in an elevated temperature will fall remarkably. This is considered for stable  $\text{LiFePO}_4$  to control surface structure destruction thermally.

[0027] thus, general formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (the inside of a formula, and M -- aluminum and B --) it is the element which contains a kind at least among Co(es). By using the positive active material which covered with  $\text{LiFePO}_4$  particle the front face of nickel multiple oxide particle with which it is expressed Structure degradation of nickel multiple oxide can be suppressed and the high capacity and the nonaqueous electrolyte cell 1 excellent in the high charge-and-discharge cycle property which combine the advantage of nickel multiple oxide that an energy density is large, and the advantage of  $\text{LiFePO}_4$  of excelling in the structural stability at the time of charge can be realized.

[0028] As a binder contained in a positive-active-material layer, the well-known resin ingredient usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.

[0029] The positive-electrode can 5 holds a positive electrode 4, and serves as an external positive electrode of the nonaqueous electrolyte cell 1.

[0030] A separator 6 can make a positive electrode 4 and a negative electrode 2 able to estrange, and the well-known ingredient usually used as a separator of this kind of nonaqueous electrolyte cell can be used, for example, high polymer films, such as polypropylene, are used. Moreover, the thickness of the relation between lithium ion conductivity and an energy density to a separator needs a thing thin as much as possible. Specifically, 50 micrometers or less are suitable for the thickness of a separator.

[0031] The insulating gasket 7 is incorporated and united with the negative-electrode can 3. This insulating gasket 7 is for preventing a break through of the nonaqueous electrolyte with which it filled up in the negative-electrode can 3 and the positive-electrode can 5.

[0032] As nonaqueous electrolyte, the solution made to dissolve an electrolyte in an aprotic non-aqueous solvent is used.

[0033] As a non-aqueous solvent, propylene carbonate, ethylene carbonate, butylene carbonate, vinylene carbonate, gamma-butyl lactone, a sulfolane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 2-methyl tetrahydrofuran, the 3-methyl 1, 3-dioxolane, methyl propionate, methyl butyrate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, etc. can be used, for example. It is desirable to use chain-like carbonate, such as annular carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, from the point of electrical-potential-difference stability especially. Moreover, such a non-aqueous solvent may be used independently, two or more kinds may be mixed and one kind may be used for it.

[0034] Moreover, as an electrolyte dissolved in a non-aqueous solvent, the lithium salt of  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  grade can be used, for example. Also in these lithium salt, it is desirable to use  $\text{LiPF}_6$  and  $\text{LiBF}_4$ .

[0035] thus, by the nonaqueous electrolyte cell 1 concerning this invention General formula  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  (M is an element which contains a kind at least among aluminum, B, and Co among a formula.) Since the positive active material which covered with  $\text{LiFePO}_4$  particle the front face of nickel multiple oxide particle with which it is expressed is used Structure degradation of nickel multiple oxide is suppressed and it becomes the high capacity and the cell excellent in the high charge-and-discharge cycle property which combine the advantage of nickel multiple oxide that an energy density is large, and the advantage of  $\text{LiFePO}_4$  of excelling in the structural stability at the time of charge.

[0036] And such a nonaqueous electrolyte cell 1 is manufactured as follows, for example.

[0037] First, the positive active material concerning this invention which was mentioned above is manufactured.

[0038] In order to make  $\text{LiFePO}_4$  particle put on the front face of  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  particle, the so-called water-solution method which forms  $\text{LiFePO}_4$  membrane surface in the front face of  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  particle can be mentioned by making the mixed water solution of the nitrate of Fe or Li, ammonium phosphate, etc. act on the  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  particle concerned, and heat-treating. In the case of this water-solution method, the homogeneity of  $\text{LiFePO}_4$  membrane surface is excellent, but  $\text{LiFePO}_4$  single phase cannot be obtained in heat treatment of those other than reducing atmosphere. If it heat-treats under reducing atmosphere,  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  particle will cause structure destruction and will carry out capacity degradation. It is difficult to obtain the positive active material which attains the object of this invention depending on a water-solution method from such a point.

[0039] On the other hand, as the adhesion approach without heat treatment, a particle hybridization method can be mentioned by dry type. Static electricity by powder object collision is generated, and a particle is made to adhere to a large drop child front face in this particle hybridization method by mixed and stirring the particle from which particle size differs. Since it does not pass through a heating process by this approach, it is possible to perform surface treatment in atmospheric air. However, since  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  particle used by this invention is weak, it tends to produce a collision crack in the above-

mentioned particle hybridization method. It depends for extent of this collision crack on the degree of hardness of  $\text{LiNi}_{1-x}\text{MxO}_2$  particle, particle size or the degree of hardness of the adhered particle  $\text{LiFePO}_4$ , and particle size. Therefore, the processing conditions by which the collision crack was controlled were required.

[0040] Then, the result of having examined wholeheartedly the conditions on which this invention person does not generate the crack of a particle and the \*\*\*\* particle  $\text{LiFePO}_4$  adheres to nickel positive-electrode particle front face, When making  $\text{LiFePO}_4$  particle put on the front face of  $\text{LiNi}_{1-x}\text{MxO}_2$  particle by the above-mentioned particle hybridization method, by making it the particle temperature  $T$  at the time of stirring processing fill the range of  $35 \text{ degrees C} \leq T \leq 45 \text{ degrees C}$  It found out that a good result could be obtained, without producing a collision crack.

[0041] The above-mentioned particle temperature  $T$  serves as an index which observes quantitatively extent of a collision of the particle at the time of stirring processing. That is, it is controlling the collision energy of a particle, and this meaning that the energy by the collision between particles controls the particle temperature  $T$  since heating and temperature rise a particle.

[0042] The particle temperature  $T$  cannot make  $\text{LiFePO}_4$  particle specifically put on the front face of  $\text{LiNi}_{1-x}\text{MxO}_2$  particle well highly [ the collision energy between particles ] enough, when lower than  $35 \text{ degrees C}$ . On the other hand, when higher than  $45 \text{ degrees C}$ , the particle temperature  $T$  will have the too large collision energy between particles, and will cause the collision crack of a particle on the contrary.

[0043] Therefore, by mixing  $\text{LiNi}_{1-x}\text{MxO}_2$  particle and  $\text{LiFePO}_4$  particle and stirring on the conditions with which the range whose particle temperature  $T$  at the time of stirring is  $35 \text{ degrees C} \leq T \leq 45 \text{ degrees C}$  is filled,  $\text{LiFePO}_4$  particle can be made to be able to put on the front face of  $\text{LiNi}_{1-x}\text{MxO}_2$  particle, without producing a particle crack, and the positive active material of this invention can be obtained.

[0044] And the nonaqueous electrolyte cell of a coin mold is produced as follows using the obtained positive active material.

[0045] as a positive electrode 4 -- first -- positive active material -- \*\* -- a binder is distributed in a solvent -- making -- the positive electrode of a slurry -- a mixture is prepared. next, the obtained positive electrode -- a positive electrode 4 is produced by applying to homogeneity, drying a mixture on a positive-electrode charge collector, and forming a positive-active-material layer. the above-mentioned positive electrode -- and also it can use a well-known binder as a binder of a mixture -- the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture.

[0046] as a negative electrode 2, a negative-electrode active material and a binder are first distributed in a solvent -- making -- the negative electrode of a slurry -- a mixture is prepared. next, the obtained negative electrode -- a negative electrode 2 is produced by applying to homogeneity, drying a mixture on a negative-electrode charge collector, and forming a negative-electrode active material layer. the above-mentioned negative electrode -- and also it can use a well-known binder as a binder of a mixture - - the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture. Moreover, the metal lithium used as a negative-electrode active material can also be used as a negative electrode 2 as it is.

[0047] Nonaqueous electrolyte is prepared by dissolving an electrolyte salt into a non-aqueous solvent.

[0048] And a negative electrode 2 is held in the negative-electrode can 3, a positive electrode 4 is held in the positive-electrode can 5, and the separator 6 which consists of porous membrane made from polypropylene etc. between a negative electrode 2 and a positive electrode 4 is allotted. Nonaqueous electrolyte is poured in into the negative-electrode can 3 and the positive-electrode can 5, and the nonaqueous electrolyte cell 1 completes the negative-electrode can 3 and the positive-electrode can 5 by fixing in total through an insulating gasket 7.

[0049] In addition, although the nonaqueous electrolyte cell 1 which used nonaqueous electrolyte was mentioned as the example and the gestalt of operation mentioned above explained it as a nonaqueous electrolyte cell, this invention is not limited to this and can be applied also about the solid electrolyte cell using the solid polymer electrolyte containing the simple substance or mixture of a conductive high

molecular compound, and the gel electrolyte cell using the gel solid electrolyte containing a swelling solvent.

[0050] Specifically, silicon, an acrylic, acrylonitrile, the poly FOSUFAZEN denaturation polymer, polyethylene oxide, polypropylene oxide, a fluorine system polymer or the compound polymer of these compounds, crosslinked polymer, a denaturation polymer, etc. are mentioned as a conductive high molecular compound contained in an above-mentioned solid polymer electrolyte and an above-mentioned gel electrolyte. As the above-mentioned fluorine system polymer, Pori (vinylidene fluoride), Pori (vinylidene fluoride-co-hexafluoropropylene), Pori (vinylidene fluoride-co-tetrafluoroethylene), Pori (vinylidene fluoride-co-truffe RUORI ethylene), etc. are mentioned.

[0051] Moreover, although the rechargeable battery was mentioned as the example and the gestalt of operation mentioned above explained it, this invention is not limited to this and can be applied also about a primary cell. Moreover, the cell of this invention is not limited especially about the configuration, and can make cylindrical, a square shape, a coin mold, a carbon button mold, etc. a thin shape and the various magnitude of large-sized \*\*.

[0052]

[Example] The example and the example of a comparison which were performed next that the effectiveness of this invention should be checked are explained. In addition, although the following examples mention and explain the concrete numeric value, it cannot be overemphasized that this invention is not what is limited to this.

[0053] <Example 1> The positive active material first applied to this invention as follows was compounded.

[0054] First, 1.0g was mixed [ 0.2OLiNi0.8Co2 particle ] with 30.0g for LiFePO4 particle. The median size of 0.2OLiNi0.8Co2 used particle was 11.458 micrometers here, and the median size of LiFePO4 particle was 0.185 micrometers. The particle-size-distribution measurement result of 0.2OLiNi0.8Co2 particle is shown in drawing 2 , and the particle-size-distribution measurement result of LiFePO4 particle is shown in drawing 3 .

[0055] Next, by stirring the mixture of 0.2OLiNi0.8Co2 particle and LiFePO4 particle for 5 minutes, LiFePO4 particle made the front face of 0.2OLiNi0.8Co2 particle cover, surface treatment was performed, and positive active material was obtained. Here, in mixed stirring of a particle, it is Nara Machine. Hybridization system Using NHS-O, rotational speed was adjusted so that the processing temperature T might become 36 degrees C.

[0056] Next, the coin mold nonaqueous electrolyte cell was produced using the positive active material obtained as mentioned above.

[0057] the obtained positive active material -- dry weight -- as 80 % of the weight and an electric conduction agent -- graphite (from the mean particle diameter of 5 micrometers to 20 micrometers: trade name KS-15 Lonza) -- as 15 % of the weight and a binder -- polyvinylidene fluoride (Aldrich #1300) -- a dimethyl full ora -- it kneaded using the id and considered as the positive-electrode paste.

[0058] Next, this \*\*\*\*\*-strike was applied on the aluminum mesh used as a positive-electrode charge collector, it pelletized with an aluminum mesh, desiccation of 1 hour was performed at 100 degrees C among the desiccation argon air current, and the positive electrode was obtained. In addition, 60mg [ per piece ] positive active material is supported by this positive electrode.

[0059] Moreover, it considered as the negative electrode by piercing a lithium metal to the above-mentioned positive electrode and of approximately the same diameter.

[0060] Moreover, LiPF6 was dissolved in the amount mixed solvent of isochore of propylene carbonate and dimethyl carbonate by the concentration of 1 mol/l, and nonaqueous electrolyte was prepared.

[0061] And the negative electrode obtained as mentioned above was held in the negative-electrode can, the positive electrode was held in the positive-electrode can, and the separator which consists of porous membrane made from polypropylene etc. between a negative electrode and a positive electrode was allotted. Nonaqueous electrolyte was poured in into the negative-electrode can and the positive-electrode can, and the nonaqueous electrolyte cell of 2025 coin molds was completed by fixing a negative-electrode can and a positive-electrode can in total through an insulating gasket.



[0062] <Example 2> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 38 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0063] <Example 3> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 40 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0064] <Example 4> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 42 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0065] <Example 5> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 44 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0066] <Example 1 of a comparison> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 30 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0067] <Example 2 of a comparison> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 34 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0068] <Example 3 of a comparison> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 46 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0069] <Example 4 of a comparison> When mixing and stirring  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle, except having adjusted rotational speed so that the particle temperature T might become 50 degrees C, positive active material was compounded like the example 1, and the nonaqueous electrolyte cell of a coin mold was produced like the example 1 using the positive active material.

[0070] <Example 5 of a comparison> Surface treatment processing to  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle was not performed, but the nonaqueous electrolyte cell of a coin mold was produced like the example 1, using the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle concerned as positive active material.

[0071] Load characteristic measurement was performed to the nonaqueous electrolyte cell produced as mentioned above. Initial charge was performed in current density  $500\mu\text{A} / \text{cel}$  until open-circuit voltage (OCV) amounted to  $4.2\text{V} \pm 0.05\text{V}$ , and discharge was performed in current density  $500\mu\text{A} / \text{cel}$  until short circuit voltage (conical cup value) amounted to  $3.0\text{V}$ .

[0072] Furthermore, \*\*\*\* was performed until OCV turned into  $4.2\text{V}$  with this current density, and 24h was saved at 60 degrees C. The same discharge as a first time cycle was performed with this current density after preservation, and the capacity was measured.

[0073] Discharge capacity before preservation was set to Cap (A), and the capacity maintenance factor was computed by the following formulas by setting discharge capacity after preservation to Cap (B).

[0074] About the nonaqueous electrolyte cell of  $\{\text{Cap (B)}/\text{Cap(A)}\} \times 100$  example 1 - an example 5 and the example 1 of a comparison - the example 5 of a comparison, the particle temperature T at the time of stirring with  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  particle and  $\text{LiFePO}_4$  particle and relation with the capacity maintenance factor (%) of a nonaqueous electrolyte cell are shown in drawing 4. [ capacity maintenance-factor (%) = ] In addition, the horizontal dotted line in drawing 4 expresses the capacity maintenance factor (%) of the example 5 of a comparison which did not perform surface treatment processing to  $0.2\text{OLiNi}_{0.8}\text{Co}_2$  particle.

[0075] Compared with the example 5 of a comparison to which the particle temperature T at the time of stirring with 0.2OLiNi0.8Co2 particle and LiFePO4 particle did not carry out surface treatment processing by the cell of the example 1 of a comparison and the example 2 of a comparison lower than 35 degrees C, the capacity maintenance factor has fallen so that clearly from drawing 4 . Since the collision energy between particles is not high enough, this is considered because LiFePO4 particle was not able to be made to put on the front face of LiNi1-xMxO2 particle well.

[0076] Moreover, the particle temperature T has fallen [ the capacity maintenance factor ] compared with the example 5 of a comparison also by the cell of the example 3 of a comparison and the example 4 of a comparison higher than 45 degrees C. This is considered for the collision energy between particles to be too large, and to have caused the collision crack of a particle on the contrary.

[0077] By the cell of an example 1 - an example 5 which, on the other hand, fills the range whose particle temperature T is 35 degrees C  $\leq$  T  $\leq$  45 degrees C, the far good capacity maintenance factor is obtained compared with the example 5 of a comparison. Since LiFePO4 particle was made to put on the front face of LiNi1-xMxO2 particle, without producing a particle crack since the collision energy between particles is controlled by the proper range, this is considered. And it turned out that the nonaqueous electrolyte cell using such positive active material becomes the thing excellent in high capacity and a high charge-and-discharge cycle property.

[0078]

[Effect of the Invention] Since LiFePO4 particle has covered the front face of nickel multiple oxide particle with which it is expressed general formula LiNi1-xMxO2 (M is an element which contains a kind at least among aluminum, B, and Co among a formula.) in this invention By suppressing structure degradation of nickel multiple oxide, becoming the positive active material which combines the advantage of nickel multiple oxide that an energy density is large, and the advantage of LiFePO4 of excelling in the structural stability at the time of charge, and using the positive active material concerned The nonaqueous electrolyte cell excellent in high capacity and a high charge-and-discharge cycle property is realizable.

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[Translation done.]